Synthesis of unsymmetrically substituted aryloxy azaphthalocyanines

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The preparation of aryloxy derivatives of azaphtalocyanines (AzaPc) is in principle quite problematic. Only two publications concerning such compounds have been published till this time. My work was focused on the synthesis of AzaPc derivatives starting from precursors bearing a functional hydroxy or carboxy group on the periphery.

Precursors were prepared by nucleophilic substitution of 5,6-dichloropyrazine-2,3-dicarbonitrile by appropriate nucleophile in the presence of base. Several preparation procedures were tested for each precursor. The procedures differ mainly in base used (NaOH, K_2CO_3, pyridine). The developed synthetic procedures were compared.

Prepared precursors underwent cyclotetramerization in quinoline with $Zn(quinoline)_2Cl_2$ heated to high temperature using hot air gun. Conditions for cyclization were optimized for each precursor. Symmetrical cyclization of precursor succeeded without difficulty. Preparation of unsymmetrical derivative containing one precursor with hydroxyl on the periphery and three precursors 5,6-di-(2,6-diisopropylphenoxy)-pyrazine-2,3-dicarbonitrile under similar conditions failed. Both precursors gave only corresponding symmetrical AzaPc.